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Introduction

Both homogeneous and phase transfer catalyzed processes have attracted considerable attention in recent years. Examples of industrial applications include the homogeneous rhodium catalyzed carbonylation of methanol to acetic acid (Monsanto process) and the hydrofornylation of propylene in an aqueous-organic two phase system [Rhone Poulenc-Ruhr Chemie].

Phase transfer catalysis usually involves an aqueous base-organic two phase system with a quaternary ammonium salt as the phase transfer agent. This technology enables one to generate anionic (or neutral) metal hydrides under exceptionally mild conditions. Once generated, such intermediates are often highly reactive towards appropriate substrates.

This contract supported research on the dearomatization of synthetic crude catalyzed by rhodium complexes. Both phase transfer and homogeneous catalysis methodology was used in this study with two samples of crude [SF-134 and SF-167] provided by EMR. The basis for this investigation was the previous finding that one could efficiently hydrogenate aromatic hydrocarbons and heterocyclic compounds by use of a metal complex and a quaternary ammonium salt as catalysts when operating in an aqueous-organic two-phase system.

Experimental

General

Two samples of synthetic crude (SF-134 and SF-167) were provided by Energy, Mines, and Resources. Chloro(1,5-hexadiene)rhodium(I) dimer was purchased from Aldrich Chemical Co., or prepared by reaction of 1,5-hexadiene with rhodium trichloride. Chlorocarbonyl bis(triphenylphosphine)rhodium chloride, hydridocarbonyltris(triphenylphosphine)rhodium, chloro(1,5-cyclooctadiene)rhodium chloride dimer, tungsten carbonyl and molybdenum carbonyl were purchased from commercial sources. The quaternary ammonium salts (cetyltrimethylammonium bromide, tetrabutylammonium hydrogen sulfate, benzyltriethylammonium chloride, Aliquat 336) were commercial products, and were used as received. PEG-400 and β-cyclodextrin were obtained from Aldrich Chemical Co. A stainless steel autoclave was used for reactions under pressure. Reactions at atmospheric pressure were run using a three-necked flask equipped with a gas inlet tube and condenser.

Analysis of the extent of dearomatization was done by C-13 nuclear magnetic resonance spectroscopy using a Varian XL-300 spectrometer.

Numerous experiments were run, with variations made in pressure, temperature, etc. (see Results and Discussion section). The following procedures are representative;

(A) A mixture of SF-167 [1.6 ml - aromatic content is 17.7% by C-13 NMR analysis], buffer pH 7.6 [5 ml,], tetrabutylammonium hydrogen sulfate [0.20 g], and the dimer of chloro(1,5-hexadiene)rhodium(I) [0.06 g.] was stirred under hydrogen for 24 hours at room temperature and one atmosphere [in a three-necked flask equipped with a gas inlet tube, stopper, and condenser]. The solution was filtered, and the phases were separated. Analysis of the synthetic crude phase revealed that the aromatic content was reduced to 15.0%. If the reaction is effected at 200 psi of hydrogen (90°C), then 27% dearomatization occurred.

(B) Desulfurization followed by dearomatization.

Silica [2 g., 250-400 mesh] was dried overnight at 400-500°C in a porcelain crucible. The cooled silica was treated with 5 ml. of a solution of tetrafluoroboric acid in diethyl ether, and then subjected to rotary evaporation. A dry hexane (60 ml.) solution containing 0.080 g [0.30 mmol] of molybdenum hexacarbonyl was added, and the solvent was

removed by rotary evaporation. The adsorbent containing molybdenum hexacarbonyl was heated at 140°C, under hydrogen, for three hours. The synthetic crude (10 ml.) was added, the mixture was heated for 60 hours at 50°C, cooled and then filtered. The desulfurized filtrate was then exposed to hydrogen and $[1,5\text{-HDRhCl}]_2$[0.06g.] for three-five days at room temperature and one atmosphere. Alternatively, the desulfurized crude, diluted with hexane (4 ml.), was treated with the same quantity of the rhodium(I) catalyst and hydrogen at 400 psi and 5[illegible]°C for 2 days. After filtration, the sample was analyzed for aromatic content by nuclear magnetic resonance spectroscopy (62-98% removal of aromatic hydrocarbons).

Results and Discussion

Initial studies with SF-134 [% aromatic : 9.7% (our analysis) - 10.6% EMR] and SF -167 [% aromatic : 17.7% (our analysis) - 17.4% EMR] were effected under phase transfer conditions using a variety of phase transfer catalysts (Table 1). See the experimental section for procedures. Examples include the following.

(a) SF-167(1.6 ml.)/$[1,5\text{-HDRhCl}]_2$ (0.06 g.)/$(C_4H_9)_4N^+HSO_4^-$ (0.20 g.)/buffer pH 7.6 (5 ml.)/H_2/r.t./1 atm./24 hours gave 15% dearomatization.

(b) Repeat of (a) for 96 hours. Addition of carbon tetrachloride (2 ml.) was made to simplify phase separation, but the same result was obtained [i.e. 15% dearomatization].

(c) Use of cetyltrimethylammonium bromide as the phase transfer agent gave 22% dearomatization, after significant separation problems due to emulsion formation.

(d) The following results were obtained with other phase transfer catalysts: Aliquat 336 [15% dearomatization of SF-134; 21% of SF-167]; dodecyltrimethylammonium chloride [10% of SF-134; 19% of SF-167]; benzyltriethylammonium chloride [4% of SF-134]; PEG-400 [16% of SF-134; 22% of SF-167]; β-cyclodextrin [12% SF-134; 12% SF-167].

(e) 27% Dearomatization resulted on repetition of (a) at 200 psi and 90°C.

The dearomatization process was also effected under homogeneous conditions. For instance, 20% dearomatization of SF-134 (4 ml.) occurred on exposure to $[1,5\text{-HDRhCl}_2]_2$[0.03 g.] and hydrogen for 1-2 days at ambient temperature. Since it was conceivable that rhodium(I) catalysts could be poisoned by sulfur present in the synthetic crude, it was decided to first treat SF-134 and SF-167 with molybdenum carbonyl pre-deposited on an acid-washed refractory oxide in order to remove most of the sulfur from the sample, with subsequent reaction with hydrogen and the rhodium catalyst.

The desulfurization of synthetic crude can occur by first washing dried Florisil or silica with tetrafluoroboric acid in ether, followed by deposition of molybdenum hexacarbonyl on the refractory oxide and then reaction with synthetic crude under hydrogen. If one now exposes the desulfurized sample to the dimer of chloro(1,5-hexadiene)rhodium(I) and hydrogen for 3-4 days at room temperature and atmospheric pressure, then complete dearomatization occurs.

A number of other rhodium catalysts were screened including chloro(1,5-cyclooctadiene)rhodium chloride dimer, chlorocarbonyl bis(triphenylphosphine)rhodium(I), and 1,5-hexadiene-1,10-phenanthroline rhodium chloride, with the latter being nearly as effective as $[1,5\text{-HDRhCl}]_2$ (Table 2). The dearomatization reaction required a long induction period. Efforts were made to enhance the efficiency of the reaction by changing one or more of the reaction parameters [i.e., after initial desulfurization]. Consider the use of higher temperatures and pressures for both samples of synthetic crude (Table 3). At 55° and 400 psi of hydrogen there is 58% dearomatization of SF-167 after two days while 37% dearomatization occurred for SF-134 under identical conditions [i.e., $H_2/[(1,5HD)Rh(1,10\text{-phen})Cl]$. Increasing the reaction temperature has a modest influence on the dearomatization process [e.g., 83% desulfurization at 90° for 2 days]. Chloro(1,5-hexadiene)rhodium(I) dimer has similar catalytic activity [50% dearomatization after two days at 25°C and 400 psi; 60% at 55° and 400 psi H_2].

As anticipated, the ease for dearomatization increases when one uses a higher concentration of the rhodium catalyst (Table 4). Use of ten times the concen- tration of $[1,5\text{-HDRhCl}]_2$ results in 90% dearomatization in 12 hours. The same proportion of dearomatization results using double the rhodium catalyst at 20°C and 400 psi.

The use of diluents such as equal volumes of either hexane, polyethylene glycol, or acetone retards the rate of dearomatization (Table 5). Furthermore, the substitution of rhodium hydrides such as hydridocarbonyltris(triphenylphos- phine)rhodium, and other cationic rhodium compounds including norbornadiene- rhodium hexafluorophosphate, for the rhodium catalysts noted above did not improve the rate of dearomatization of synthetic crude.

All attempts to effect concurrent desulfurization and dearomatization of synthetic crude met with little success. The following catalytic systems ave inferior results to the two step sequence of desulfurization followed by dearomatization: (a) $[1,5\text{-HDRhCl}]_2/Mo(CO)_6$ on SiO_2/HBF_4; (b) $[1,5\text{-HDRhCl}]_2/Mo(CO)_6$ on Florisil/HBF_4; (c) $[1,5\text{-HDRhCl}]_2/W(CO)_6$ on SiO_2/HBF_4; (d) [(1,5HD)Rh(1,10-phenanthroline)Cl]/$Mo(CO)_6$-SiO_2/HBF_4.

Conclusions and Recommendations

Moderate dearomatization of synthetic crude can be achieved by the use of rhodium(I) catalysts operating under phase transfer or homogeneous conditions. The dearomatization is complete, provided the synthetic crude is first subjected to desulfurization by the use of molybdenum carbonyl pre-deposited on acid washed silica or Florisil. There is a considerable induction period prior to dearomatization. One can assume that the induction period is related to the time required to generate the catalytically active metal hydride. The most effective rhodium catalysts are the dimer of chloro(1,5-cyclooctadiene)rhodium and cationic 1,5-hexadiene-1,10-phenanthrolinerhodium chloride. The use of high concen- trations of either of these catalysts results in efficient dearomatization but, considering the high cost of rhodium, this process has no commercial potential.

In summary, unless one is able to achieve dearomatization without prior desulfurization, this rhodium(I) catalyzed reaction, although novel in concept and simple in execution, has little, if any, commercial potential.

Table 1

Effect of Phase Transfer Catalyst on Dearomatization of SF-134 and SF-167[a]

Phase Transfer Agent	Sample of Crude	% Dearomatization
$(C_4H_9)_4N^+HSO_4^-$	SF-167	15
	SF-167	27[b]
$C_{12}H_{25}N(CH_3)_3^+Cl^-$	SF-134	10
	SF-167	19
Aliquat 336	SF-134	15
	SF-167	21
$C_6H_5CH_2N(C_2H_5)_3^+Cl^-$	SF-134	4
$C_{16}H_{33}N(CH_3)_3^+Br^-$	SF-167	22
PEG-400	SF-134	16
	SF-167	22
β-Cyclodextrin	SF-134	12
	SF-167	12

[a] Using procedure A in experimental section. [b] Reaction effected at 200 psi and 90°C.

Table 2

Effect of Metal Catalyst on the Dearomatization Process[a]

Metal Catalyst	Sample of Crude	% Dearomatization
$[1,5\text{-HDRhCl}]_2$	SF-134	>98
	SF-167	92
$[1,5\text{-CODRhCl}]_2$	SF-134	77
$(Ph_3P)_2Rh(CO)Cl$	SF-134	40
	SF-167	44
[1,5-HDRh(1,10-phen)Cl]	SF-134	77
	SF-167	80
$HRh(CO)(PPh_3)_3$	SF-134	50
	SF-167	58
$(NBD)_2RhPF_6$	SF-134	15
	SF-167	17

[a] Using procedure B at room temperature for 4-5 days.

Table 3

Influence of Temperature and Pressure on Homogeneous Dearomatization Process[a]

Metal Catalyst	Sample	T, °C	Pressure	% Dearomatization
[(1,5-HD)Rh(1,10-phen)Cl]	SF-167	r.t.	1 atm.	34
		55	400 psi	58
		90	400 psi	83
	SF-134	r.t.	1 atm.	27
		55	400 psi	37
$[1,5\text{-HDRhCl}]_2$	SF-167	r.t.	400 psi	50
		55	400 psi	62
		100	600 psi	> 98[b]
	SF-134	r.t.	400 psi	61
		55	400 psi	68
		55	900 psi	87
		85	900 psi	96

[a] Using procedure B for two days reaction time. [b] 72 hours.

Table 4

Effect of Concentration of $[1,5\text{-HDRhCl}]_2$ on the Dearomatization Process[a]

Amount in g	Sample	Temp. °C	Rx time, h	Pressure	% Dearomatization
0.06	SF-167	r.t.	48	1 atm.	38
0.06	SF-167	r.t.	48	400 psi	50
0.12	SF-167	r.t.	24	400 psi	88
0.6	SF-167	r.t.	12	1 atm.	90
0.06	SF-134	r.t.	48	1 atm.	41
0.06	SF-134	r.t.	48	400 psi	61
0.12	SF-134	r.t.	24	400 psi	86
0.3	SF-134	r.t.	12	1 atm.	63
0.6	SF-134	r.t.	12	1 atm.	93
0.6	SF-134	r.t.	48	1 atm.	> 98

[a] Procedure B.

Table 5

Influence of Equal Volumes of Diluents on Dearomatization

Sample	Metal Catalyst	Diluent	% Dearomatization
SF-134	$[1,5\text{-HDRhCl}]_2$	Acetone	22
	$[1,5\text{-HDRhCl}]_2$	Polyethylene glycol	16
		Toluene	30
SF-167	$[1,5\text{-HDRhCl}]_2$	Acetone	10
	$[1,5\text{-HDRhCl}]_2$	Toluene	48
	$[1,5\text{-CODRhCl}]_2$	Toluene	45